In subsequent runs the yield was the same when zinc powder was omitted. Washing the diazonium salt on the filter with water dissolves part of it. If the wash water is run into the acidic filtrate, the salt crystallizes again in long white needles.

Nitration of this product (0.1 g.) with sulfuric–nitric acid mixture (3:2) at 0° gave methyl 6,8-dinitrodehydroabietate (0.05 g.), m. p. 185.5–188° after one crystallization from acetone–methanol. Mixed with pure dinitro ester the melting point was 187–188.5°.

Nitration Experiments on the Sulfonic Acids.—(a) To a solution of 4.35 g. of sulfonic acid trihydrate in 15 cc. of concentrated sulfuric acid, was added 0.65 cc. of concentrated nitric acid at ice-salt temperature. After stirring for fifteen minutes, the mixture was poured into 75 cc. of ice and water and the gelatinous precipitate was filtered and washed with a mixture of 35 cc. of concentrated hydrochloric acid and 70 cc. of water. Air-dried at 50° overnight, the product weighed 4.7 g. (calcd. for anhydrous sulfo-nitro acid, 4.25 g.). This product was boiled with 500 cc. of water and on filtration gave 0.12 g. (3%) of water insoluble material. By evaporation of the filtrate to dryness, 4.6 g. of water-soluble material was recovered.

The water-insoluble part was identified as 6,8-dinitrodehydroabietic acid by conversion to the methyl ester with diazomethane. There was obtained 0.08 g. which melted at 187.5–188°. Mixed with an authentic sample, the melting point was 188–188.5°.

One gram of the water-soluble part was dissolved in a few cc. of methanol and treated with excess diazomethane in ether. During this reaction the ester, which is only slightly soluble in ether, separated as a fine white crystalline precipitate, 0.65 g., m. p. 238.5–240°. A second crop of 0.15 g., m. p. 235–236.5°, was obtained on concentrating the ether solution, bringing the total yield to 81%. One crystallization from acetone gave pure dimethyl ester, m. p. 243.5–244°. The melting point of a mixture with the dimethyl ester of the sulfo-nitro acid of Hasselstrom and Hopkins[5] was the same.

(b) One gram of the 6-sulfo acid trihydrate was stirred into a mixture of 4 cc. of concentrated sulfuric acid and 2 cc. of concentrated nitric acid with cooling in an ice–salt-bath. After twenty minutes the mixture was poured into 30 to 40 cc. of ice and water, and worked up as above. The water-insoluble material weighed 0.2 g. (22%) and gave 0.17 g. of methyl 6,8-dinitrodehydroabietate, m. p. 185–186.5°, which melted at 187–188° when mixed with a known sample.

(c) Treatment of 1.0 g. of the sulfo-nitro acid prepared in (a) with mixed acids as described in part (b) gave only a trace (about 0.02 g.) of water-insoluble material.

Summary

1. The sulfonic acid group in sulfodehydroabietic acid and in the nitro-sulfo derivative has been shown to be located at position 6. The same position is occupied by one of the nitro groups of the dinitro derivative.

2. The 6-amino and 6-hydroxy derivatives of dehydroabietic acid have been prepared by a new method which makes these substances easily available in quantity.

3. The 8-nitro derivative, which is to be used for the preparation of the corresponding hydroxy and amino compounds, has been prepared.

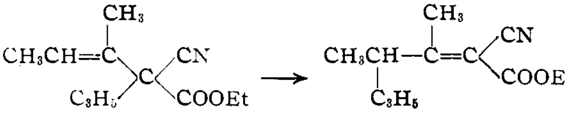
CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 12, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Rearrangement of Allyl Groups in Three-Carbon Systems. I.[1]

BY ARTHUR C. COPE,[2] KATHRYN E. HOYLE AND DOROTHEA HEYL

It was reported recently that ethyl (1-methylpropenyl)-allylcyanoacetate rearranged on heating to ethyl (1,2-dimethyl-4-pentenylidene)-cyanoacetate.[3]



This α,γ-shift of an allyl group in a three-carbon system involves structural changes similar to those occurring in the familiar Claisen rearrangement of allyl phenol, enol and vinyl ethers. This paper describes work undertaken to determine whether the rearrangement is general for appropriately substituted three-carbon systems, just as the Claisen rearrangement is general for the $\rangle C{=}\underset{|}{C}{-}OC_3H_5$ system.

By alkylation methods previously described,[4] six cyanoacetic esters, four malonic esters and two malononitriles were prepared, each disubstituted by an alkyl vinyl and an allyl group. All of these compounds rearranged on heating, and in all but two cases the rearrangements were relatively free from side reactions, so that pure products could be isolated. It was considered important to prove

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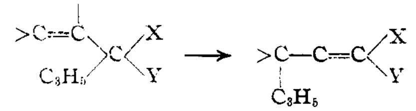
[1] Supported by a grant from the Penrose Fund of the American Philosophical Society.

[2] A. C. C. is indebted to the John Simon Guggenheim Memorial Foundation for the award of a fellowship in the general field of this investigation.

[3] Cope and Hardy, THIS JOURNAL, 62, 441 (1940).

[4] Cope and Hoyle, *ibid.*, 63, 733 (1941), and preceding papers.

the structure of each of the rearrangement products beyond question, rather than to assume that the reactions followed the course of the single rearrangement studied previously. This was done either by cleavage of the isomerization products with ammonia to ketones which could be identified by direct comparison, by independent synthesis of the rearrangement products, or by their reduction and conversion to solid derivatives which could be compared with known samples. By these methods it was established that in each case the allyl group had shifted from the α- to the γ-carbon atom, while the double bond shifted from the β,γ- to the α,β-position.

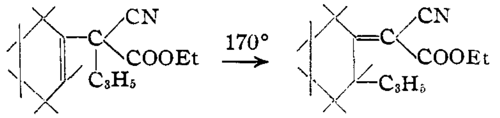


(X and Y = CN or COOEt)

Cyanoacetic Ester Series.—This series was extended in order to discover whether the rearrangement followed the same course as the original example[3] when the substituted vinyl group was more complex in structure.

Ethyl 1-cyclohexenylallylcyanoacetate, I, was prepared by the alkylation of ethyl cyclohexylidene cyanoacetate with allyl bromide. The ester did not rearrange during distillation at low pressures; b. p. 110–111° (1 mm.).

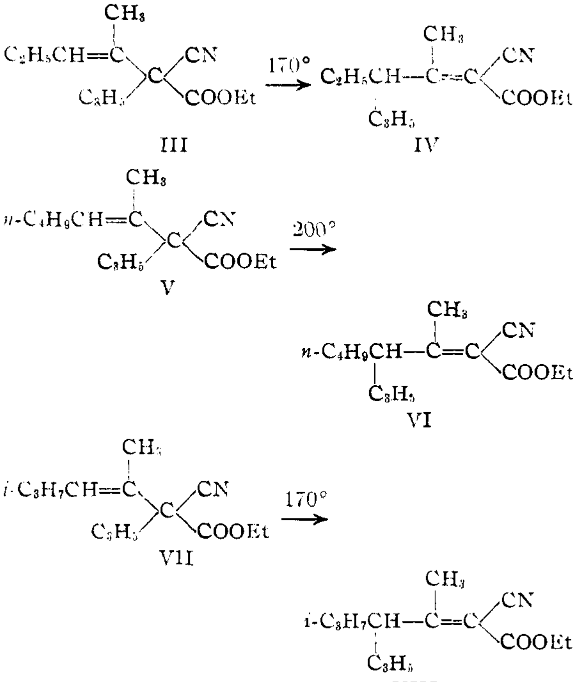
Compound I was isomerized by refluxing for eight to ten hours at pressures regulated so that the temperature of the boiling liquid was 230, 200 and 170°. The least decomposition occurred and the purest product was obtained at 170°. The structure of the product, ethyl (2-allylcyclohexylidene)-cyanoacetate, II, was proved by its cleavage with concentrated aqueous ammonia, a reaction which appears to be general for *s*-alkylidene cyanoacetic esters. The cleavage produced the known ketone, 2-allylcyclohexanone, which was completely identified by preparation of the oxime and its comparison with a known sample. The structure of II was also verified by synthesizing a known sample from 2-allylcyclohexanone and ethyl cyanoacetate.



I II

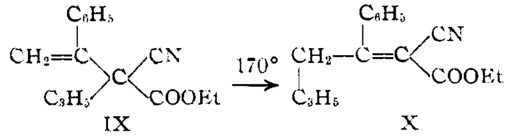
In this case, as in the others described below, the purity of the initial alkylation product was indicated by its normal molecular refraction (calcd. for I, 65.21, found 65.51). During each of the rearrangements the refractive index increased; for example, $n^{25}\mathrm{D}$ of I was 1.4820; of II, 1.4980. The rearrangement products contain conjugated systems and exhibit an exaltation in molecular refraction: $M\mathrm{D}$ calcd. for II 65.21, found 66.73, exaltation 1.52.

By similar methods, three (1-methyl-2-alkylvinyl)-allylcyanoacetic esters, III, V and VII were prepared and rearranged by heating to IV, VI and VIII. The structures of the rearrangement products were established by their cleavage with ammonia to *unsym*-alkyl allylacetones. The identity of the three ketones was established by direct comparison with known samples which were prepared by the acetoacetic ester synthesis, and by comparison of the 2,4-dinitrophenylhydrazones of the ketones from the two sources.



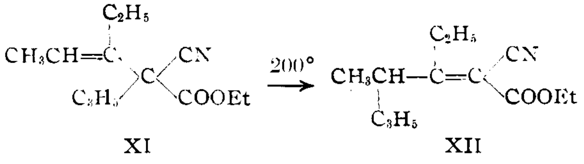
III IV V VI VII VIII

Ethyl (1-phenyl-vinyl)-allylcyanoacetate (IX) rearranged very readily on heating to X. Since IX is quite high boiling, it could be obtained pure only by distillation in the high vacuum produced by a mercury vapor pump. Both IX and X con-



IX X

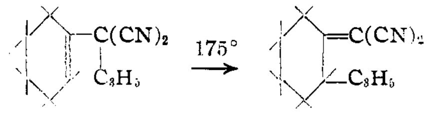
tain conjugated double bonds. Extension of the conjugation increased the exaltation in molecular refraction from 1.54 (IX) to 2.99 (X). X was identified by cleavage with ammonia to ω-allylacetophenone, from which the oxime and semicarbazone, both known compounds, were prepared.


$$CH_3CH{=}\overset{C_2H_5}{C}\!\!\begin{smallmatrix}\\\\\end{smallmatrix}{>}C{<}\begin{smallmatrix}CN\\COOEt\end{smallmatrix}\ (C_3H_5) \xrightarrow{200°} CH_3\underset{C_3H_5}{CH}{-}\overset{C_2H_5}{C}{=}C{<}\begin{smallmatrix}CN\\COOEt\end{smallmatrix}$$

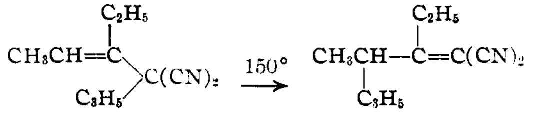
XI XII

The ester XI also rearranged normally into XII, whose structure was established by cleavage with ammonia to α-allyl diethyl ketone. A known sample of this ketone was prepared by the direct alkylation of diethyl ketone by the Haller-Bauer method. The 2,4-dinitrophenylhydrazones of the ketones from the two sources were identical.

Malononitrile Series.—1-Cyclohexenyl-allylmalononitrile (XIII) and 1-ethylpropenyl-allylmalononitrile (XV) were prepared by alkylating the alkylidene malononitriles.[4] Both of these compounds rearrange extremely easily, and could be purified by distillation only in very high vacuum. The structures of the rearrangement products (XIV and XVI) were verified by cleavage with concentrated aqueous ammonia to 2-allylcyclohexanone and α-allyl diethyl ketone, respectively.

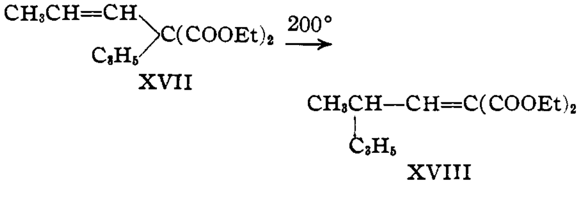


XIII XIV


$$\begin{smallmatrix}CH_3CH{=}\overset{C_2H_5}{C}\\C_3H_5\end{smallmatrix}{>}C(CN)_2 \xrightarrow{150°} CH_3\underset{C_3H_5}{CH}{-}\overset{C_2H_5}{C}{=}C(CN)_2$$

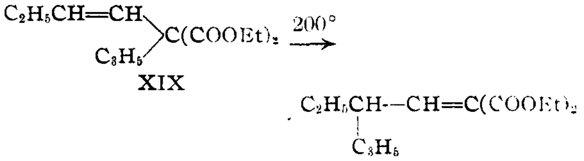
XV XVI

Malonic Ester Series.—Ethyl propenylallylmalonate (XVII) rearranged in good yield to the ethyl (2-methyl-4-pentenylidene)-malonate, XVIII. XVIII was characterized by quantitative hydrogenation, which produced ethyl (2-methyl-pentyl)-malonate. A known sample of the latter ester, prepared by reducing ethyl (2-methylpentylidene)-malonate, had the same physical properties, and both samples gave identical specimens of 5-(2-methylpentyl)-barbituric acid on condensation with urea.


$$\begin{smallmatrix}CH_3CH{=}CH\\C_3H_5\end{smallmatrix}{>}C(COOEt)_2 \xrightarrow{200°} CH_3\underset{C_3H_5}{CH}{-}CH{=}C(COOEt)_2$$

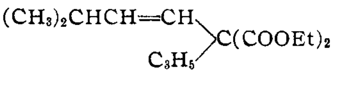
XVII XVIII

The next higher homolog, ethyl (1-butenyl)-allylmalonate, XIX, rearranged in the same way to XX, which was also identified by reduction, followed by conversion of the reduced ester to 5-(2-ethyl-pentyl)-barbituric acid.

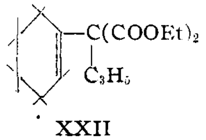

$$\begin{smallmatrix}C_2H_5CH{=}CH\\C_3H_5\end{smallmatrix}{>}C(COOEt)_2 \xrightarrow{200°} C_2H_5\underset{C_3H_5}{CH}{-}CH{=}C(COOEt)_2$$

XIX XX

Two esters of higher molecular weight, ethyl isopentenylallylmalonate (XXI) and ethyl (1-cyclohexenyl)-allylmalonate (XXII) rearranged on heating, but did not give pure products.


$$\begin{smallmatrix}(CH_3)_2CHCH{=}CH\\C_3H_5\end{smallmatrix}{>}C(COOEt)_2$$

XXI



XXII

In both cases the products obtained by heating the esters until the refractive index became constant were mixtures which did not have constant boiling points. The product obtained from XXII yielded 2-allylcyclohexanone on cleavage with ammonia, proving the presence of the normal isomerization product in the mixture.

It may be concluded that this rearrangement of allyl groups in acyclic or alicyclic three carbon systems is a quite general reaction when the α-carbon atom is attached to two CN or COOEt groups, or to one of each of these groups. Side reactions of unknown character occur during the rearrangement of the higher homologs in the malonic ester series, and to a smaller extent in the cyanoacetic ester series if the isomerizations are carried out at superoptimal temperatures.

Work designed to reveal additional facts concerning the extent to which the three-carbon system must be activated by attachment to "negative" or electron attracting groups for the rearrangement to occur is in progress.

Rates of Rearrangement.[5]—The process of rearranging the substituted vinyl allyl compounds

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(5) We are indebted to Dr. Farrington Daniels and Dr. James L. Crenshaw for advice concerning the kinetic studies. A more thorough investigation of the kinetics of the rearrangements which proceed most cleanly will be made later.

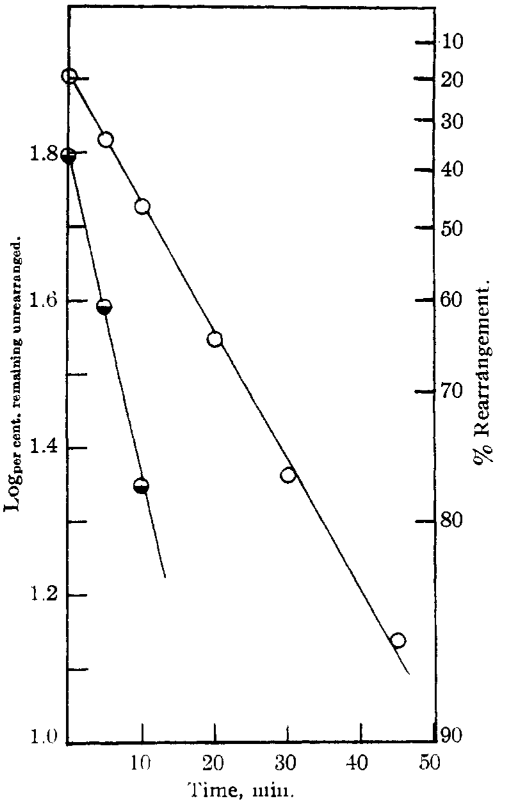

Fig. 1.

by successive periods of heating followed by distillation was well suited to the purpose of isolating pure rearrangement products, but furnished little information concerning the rates of the isomerizations. In many cases the rearrangement was complete after the first period of heating. It was found possible to determine the rates of rearrangement very simply by observing the change in refractive index of each of the substances with time at a suitable temperature. The rates furnish significant information concerning the mechanism of the isomerization, and reveal the influence of structural factors upon the relative ease of rearrangement.

Pyrex tubing (5 mm. o. d.) was cut into 8-cm. lengths which were sealed at one end, soaked in a solution of potassium dichromate in sulfuric acid, thoroughly rinsed and dried. Four or five drops of the sample for rearrangement were introduced, after which the tube was evacuated to a pressure of 30 mm. and sealed. A fine wire was attached to a hook left on the end of the seal, so that the tube could be handled easily. Eight to ten such tubes were prepared for each compound, and all were dropped at the same time into a small glass thermostat kept at temperatures of 135.7, 176.5 or 193.1 ± 0.5° by heating with the vapor of refluxing ethylbenzene, *p*-cymene and decalin, respectively. The time at which the thermostat regained constant temperature (after a lag of eight to eleven minutes) was called zero time. A sample was removed at this time, cooled, and its refractive index determined. Successive samples were removed at definite times until the refractive index became constant.

The kind of data obtained is illustrated by Table I, which shows the rate of rearrangement of 1-cyclohexenyl allylmalononitrile (XIII).[6] The agreement of the first order rate constants for successive time intervals as the isomerization proceeded (Table I) shows that the rearrangement of XIII is a first order reaction. Similar kinetic data for the remaining rearrangements prove that nine of the ten isomerizations are unimolecular. The evidence is summarized in Figs. 1, 2 and 3, in which $\log_{\text{per cent. remaining unrearranged}}$ is plotted against time for each isomerization. The points fall close to the best straight line drawn through them in each case, while separate plots of 1/fraction remaining unrearranged against time (not shown) gave definitely curved lines except for compound XIX. The rate of rearrangement of XIX is in somewhat better agreement with first than with second order kinetics, but the difference is not significant. The rate measurements on XIX were probably inexact because of the occurrence of side reactions affecting the refractive index.

TABLE I

RATE OF REARRANGEMENT OF 1-CYCLOHEXENYL ALLYLMALONONITRILE AT 135.7 ± 0.5°

Time, min.	n^{25}D[b]	%[c] rearrangement	1/Fraction unrearranged	Log per cent. unrearranged	k unimolecular[d] min.$^{-1}$
0[a]	1.4916	19.8	1.25	1.904	
5	1.4957	34.2	1.52	1.818	0.040
10	1.4992	46.7	1.88	1.727	.042
20	1.5043	64.7	2.84	1.548	.041
30	1.5078	77.0	4.35	1.362	.043
45	1.5104	86.3	7.30	1.137	.034
100	1.5140	99.0			
121	1.5142	100			
150	1.5143	100			

[a] Time at which the thermostat regained the temperature of 135.7° after a lag of ten minutes. [b] Initial n^{25}D was 1.4860. [c] Calculated from (n − n initial)/(n final − n initial) × 100. [d] Calculated from the formula: $k = \frac{1}{t_2 - t_1} 2.303 \log \frac{1 - x_1}{1 - x_2}$; x_1 and x_2 = fraction of material rearranged at t_1 and t_2.

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(6) XIII gave the best kinetic data of the compounds studied.

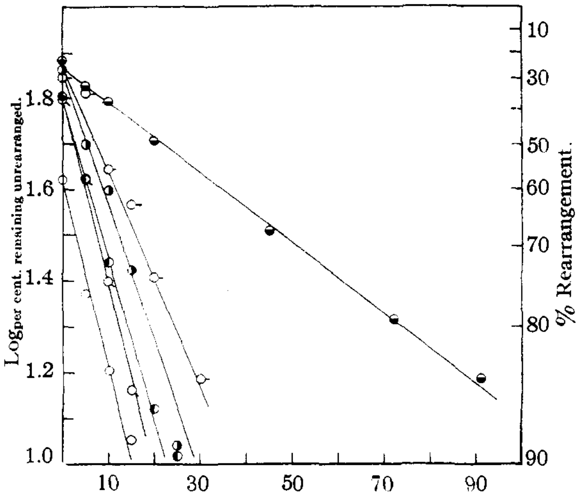

Fig. 2.

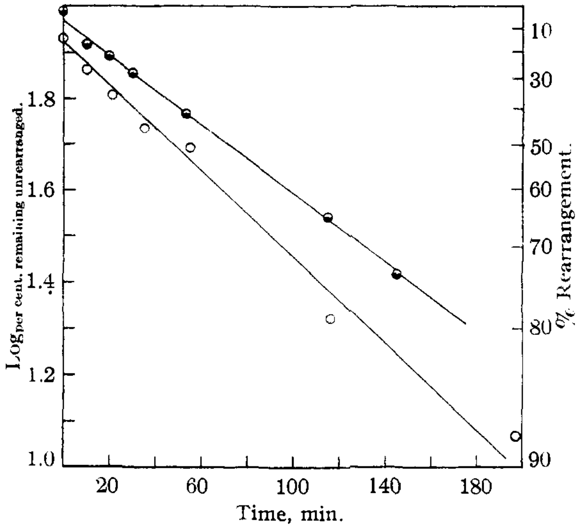

Fig. 3.

Correspondence of the rates to first order kinetics is strong evidence that the rearrangements are intra- rather than intermolecular.[7]

The logarithmic scale at the right of Figs. 1, 2 and 3 shows directly the per cent. rearrangement of each compound at the times indicated on the horizontal axis. A convenient measure of the relative rates of the isomerizations is given by the first order rate constants, calculated from 2.303 × slope of each line. These figures are assembled in Table II, in the order of decreasing rates of rearrangement. The most striking difference in rates exists between the malononitriles, which rearrange much faster than the cyanoacetic esters, which in turn isomerize faster than the malonic esters.

TABLE II

UNIMOLECULAR RATE CONSTANTS

Compd. rearranged	Temp., °C.	Deviation of final n^{25}D from true n^{25}D[a]	k, min.$^{-1}$
XV	135.7	−0.0003	0.10
XIII	135.7	none	.040
IX	176.5	− .0001	.096
XI	176.5	− .0010	.092
III	176.5	− .0009	.081
I	176.5	+ .0002	.068
V	176.5	none	.055
VII	176.5	− .0005	.018
XIX	193.1	− .0008	.011
XVII	193.1	− .0010	.0086

[a] These figures show the deviation of the final refractive index of the samples heated in tubes from the true refractive index of the pure rearrangement products. The close correspondence indicates that the isomerizations were essentially complete and that side reactions occurred to a very small extent. The final rather than the true n^{25}D was used in calculating the data graphed in Figs. 1, 2 and 3.

The great difference in ease of isomerization of the three classes made it necessary to operate at three different temperatures in order to obtain complete isomerizations in convenient lengths of time. The difference was confirmed by rearranging 1-cyclohexenylallylmalononitrile (XIII), ethyl 1-cyclohexenyl-allylcyanoacetate (I) and ethyl propenyl-allylmalonate (XVII) at the same temperature, 176.5°. At zero time (after the thermostat regained constant temperature; see above) the rearrangement of XIII was 96.5% and at five minutes 100% complete; at the same times I had rearranged to the extent of 27 and 50%, while after fifteen minutes the isomerization of XVII amounted to only 1.8%.

These results are in accord with the concept (generally accepted for the Claisen rearrangement)[8] that one motivating force responsible for the rearrangement is the unequal sharing of the electron pair binding the allyl group to the atom to which it is attached. In the isomerization, the allyl group becomes detached from this atom, and recombines with the atom in the γ-position, which is less electron attracting. It is evident that the influence causing the detachment of the allyl group in the cases herein described is the electron attraction of the α-carbon atom, and the tendency to form a stable conjugated system of double bonds. Since the nitrile group is more electron

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(7) *Cf.* Kincaid and Tarbell, THIS JOURNAL, **61**, 3085 (1939), for a kinetic study of the Claisen rearrangement; also ref. 3 and the following paper concerning the mechanism of the rearrangement of allyl groups in the three-carbon system.

(8) See Tarbell, *Chem. Rev.*, **27**, 495 (1940).

attracting than carbethoxyl, the electron attraction of the α-carbon atom decreases in the order: malononitrile > cyanoacetic ester > malonic ester. Any steric effect tending to block the rearrangement by preventing the end of the allyl group from coming in proximity to the γ-carbon atom would lead to the same order, since the carbethoxyl group is larger than the nitrile group.

Much smaller differences in relative ease of rearrangement exist within the three series. The only definite correlation which can be made is that steric hindrance by large or branched groups on the γ-carbon atom retards the isomerizations. The cyanoacetic esters which rearrange fastest are either unsubstituted on the γ-carbon atom (IX), or substituted in that position by methyl or ethyl groups (XI, III), or are unhindered in the γ-position because of the presence of a ring (I). The cyanoacetic ester rearranging most slowly has the branched isopropyl group in the γ-position (VII).

Experimental Part[9]

The alkylation methods previously described as the most advantageous for the cyanoacetic ester[10] and malonic ester[11] series were employed in preparing the substituted vinyl allyl compounds, except that ethyl alcohol was used as the solvent to avoid the formation of mixtures by re-esterification. Each of the alkylation products was first purified by distillation, and the yield of distilled material with approximately the correct refractive index is reported for each preparation. Further purification was accomplished by treatment with 20% sodium bisulfite in the cyanoacetic ester and malononitrile[4] series, and by refractionation in each case. The distillations were carried out at pressures low enough to avoid rearrangement. The absence of the corresponding rearrangement product in each purified substance was verified either by the fact that the middle and last fractions had the same refractive index, or by identity in refractive index of the middle fractions in successive distillations.

In the thermal rearrangements, the substituted vinyl allyl compounds were placed in a two-necked flask attached to a small Widmer column. The column was connected to a vacuum system containing a large reservoir and a variable leak, so that the pressure and consequently the boiling point of the liquid (measured by a thermometer whose bulb was immersed in the liquid) could be regulated. The liquids were refluxed at temperatures of 150 to 230° for periods of one to seven hours, the column being used as a reflux condenser. They were then distilled and separated into three fractions: (1) a fore-run of 1 to 3 g., (2) the main portion, usually 10 to 30 g., (3) the hold-up of the column, which was distilled by reducing the pressure with an oil pump. After the refractive indexes of the fractions were determined, they were combined and again heated and distilled in the same manner. The process was repeated until the refractive index of the middle fraction remained constant within 0.0005 unit, which indicated that the rearrangement was complete, since all of the rearrangement products have higher refractive indexes than the starting materials. The product was then fractionally distilled in the usual manner, the criteria of homogeneity being constancy of boiling point and particularly of refractive index.

Ethyl 1-Cyclohexenyl Allylcyanoacetate (I).—The alkylation of the sodium enolate prepared from 48.3 g. of ethyl cyclohexylidene-cyanoacetate[12] and sodium ethoxide with allyl bromide gave 46.1 g. (79%) of I, which after purification as described above had the following properties: b. p. 110–111° (1 mm.); $n^{25}\text{D}$ 1.4820; d^{25}_{25} 1.0183; *M*D calcd. 65.21, found 65.51.

Anal. Calcd. for $C_{14}H_{19}O_2N$: N, 6.00. Found: N, 5.87.

Ethyl (2-Allylcyclohexylidene)-cyanoacetate (II).—When I was refluxed at 230° and at 200° for eight to nine hours, side reactions accompanied the rearrangement. A white solid which sublimed into the receiver during the final distillations was formed, and the distillates were yellow and had a tobacco-like odor. At 170° I (17 g.) was completely rearranged after ten hours to give 15 g. of II, a colorless liquid, b. p. 170–171° (13 mm.); $n^{25}\text{D}$ 1.4980; d^{25}_{25} 1.0276; *M*D calcd. 65.21, found 66.74, exaltation 1.53.

Anal. Calcd. for $C_{14}H_{19}O_2N$: N, 6.00. Found: N, 5.93.

II (6 g.) was cleaved by shaking with 60 cc. of concentrated aqueous ammonia for twenty-four hours. Extraction with ether and distillation gave 2.7 g. (76%) of 2-allylcyclohexanone, b. p. 83–84° (13 mm.), $n^{25}\text{D}$ 1.4666, m. p. of the oxime and mixed m. p. with a known sample described below 69.5–70°.

2-Allylcyclohexanone.—Ethyl 2-ketocyclohexanecarboxylate was prepared approximately as by Kötz and Michels[13] by condensing cyclohexanone with ethyl oxalate and heating the oxalo ester. The loss of carbon monoxide was complete only after the oxalo ester was heated for three hours in vacuum at 150–180°; yield 60%. The alkylation of 55 g. of this ester in the usual manner with allyl bromide in ethyl alcohol gave 60.6 g. (89%) of ethyl 1-allyl-2-ketocyclohexanecarboxylate, b. p. 135–136° (16 mm.); $n^{25}\text{D}$ 1.4652. The latter ester is difficult to hydrolyze. Stirring for five hours at room temperature, five hours at 60° and twelve hours at 80° with 5% aqueous potassium hydroxide hydrolyzed about one-third of the ester, while the remainder was recovered in a very pure state; b. p. 127–128° (11 mm.); $n^{25}\text{D}$ 1.4658; d^{25}_{25} 1.0307; *M*D calcd., 56.64, found, 56.64.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.72; H, 8.75.

The hydrolysis was completed by refluxing the keto ester with 5% potassium hydroxide for forty-two hours and refluxing the ester recovered from this operation with 10% potassium hydroxide for the same period. The total yield

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[9] All melting and boiling points are uncorrected.

[10] Cope and Hancock, THIS JOURNAL, **60**, 2903 (1938).

[11] Cope, Hartung, Hancock and Crossley, *ibid.*, **62**, 314 (1940).

[12] Cope, *ibid.*, **59**, 2327 (1937).

[13] Kötz and Michels, *Ann.*, **350**, 210 (1906); Kötz, *ibid.*, **358**, 198 (1908).

of 2-allylcyclohexanone from 60.6 g. of ester was 26 g. (66%), b. p. 78–79° (11 mm.); n^{25}_D 1.4662; m. p. of the oxime (recrystallized from dilute alcohol), 70–70.5°. This ketone was prepared by direct alkylation by Cornubert,[14] who also prepared its oxime.

Direct Synthesis of II.—2-Allylcyclohexanone (21 g.), ethyl cyanoacetate (17 g.), ammonium acetate (2.3 g.), acetic acid (7.2 g.) and benzene (30 cc.) were refluxed under a constant water separator for four hours. After cooling, washing with water and distilling, 25 g. (71%) of II was obtained, b. p. 124–125° (1.5 mm.); n^{25}_D 1.5008; d^{25}_{25} 1.0280; M_D calcd. 65.21, found 67.04, exaltation 1.83. These properties differ slightly from those of II prepared by the rearrangement of I. In order to see if this difference might be due to a different ratio of the two possible geometric isomers of II, a sample of the synthetic ester (9.2 g.) was refluxed for one hour at 200° in vacuum. Considerable high boiling material was formed, but 6.1 g. of the ester was recovered. The middle fraction of the recovered ester (4 g.) had n^{25}_D 1.4979; d^{25}_{25} 1.0285. This change in properties produced by heating is explained reasonably by a change in the ratio of the two geometric isomers. Nitrogen analyses of the synthetic ester both before and after heating agreed with the theoretical value.

Ethyl (1-Methyl-1-butenyl)-allylcyanoacetate (III).—The alkylation of 45.3 g. of ethyl (1-methylbutylidene)-cyanoacetate with allyl bromide gave 32 g. (58%) of III; after purification b. p. 91–92° (1 mm.); n^{25}_D 1.4580; d^{25}_{25} 0.9603; M_D calcd. 62.79, found 63.07.

Anal. Calcd. for $C_{13}H_{19}O_2N$: N, 6.33. Found: N, 6.18.

Ethyl (1-Methyl-2-ethyl-4-pentenylidene)-cyanoacetate (IV).—III (22.5 g.) heated for eight hours at 170° gave 18.3 g. of IV, b. p. 160–161° (21 mm.); n^{25}_D 1.4770; d^{25}_{25} 0.9714; M_D calcd. 62.79, found 64.56, exaltation 1.77.

Anal. Calcd. for $C_{13}H_{19}O_2N$: N, 6.33. Found: N, 6.29.

IV (8 g.) on shaking with 80 cc. of concd. ammonia for twenty-four hours followed by extraction with ether and distillation gave 3.5 g. (77%) of *unsym*-ethylallylacetone, b. p. 155–156°; n^{25}_D 1.4260; m. p. of the 2,4-dinitrophenylhydrazone and mixed m. p. with a known sample 51–53°.

Anal. of the 2,4-dinitrophenylhydrazone. Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.29. Found: N, 18.06.

***unsym*-Ethylallylacetone.**—The alkylation of ethyl allylacetoacetate[15] (61.2 g.) with ethyl iodide gave 53.6 g. (75%) of ethyl ethylallylacetoacetate, b. p. 118–119° (23 mm.); n^{25}_D 1.4420; d^{25}_{25} 0.9739; M_D calcd. 54.21, found 54.02.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.81; H, 9.30.

The above ester (40 g.) was refluxed with 275 cc. of 5% potassium hydroxide for seven days. On extraction with ether and distillation 4 g. of the ester was recovered, while the yield of *unsym*-ethylallylacetone was 12.2 g. (48%); b. p. 150–152°; n^{25}_D 1.4260; d^{25}_{25} 0.8388; M_D calcd. 38.70, found 38.66.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.00; H, 11.40.

The m. p. of the 2,4-dinitrophenylhydrazone was 51.5–53°.

Ethyl (1-Methyl-1-hexenyl)-allylcyanoacetate (V).—Ethyl 1-methylhexylidenecyanoacetate (52.3 g.) alkylated with allyl bromide gave 32.5 g. (52%) of V; after purification, b. p. 106–107° (1 mm.); n^{25}_D 1.4614; d^{25}_{25} 0.9456; M_D calcd. 72.03, found 72.62. (The high M_D found may indicate slight rearrangement during distillation.)

Anal. Calcd. for $C_{15}H_{23}O_2N$: N, 5.62. Found: N, 5.51.

Ethyl (1-Methyl-2-butyl-4-pentenylidene)-cyanoacetate (VI).—V (16.2 g.) heated for nine hours at 200° gave 12.4 g. of VI, b. p. 173–174° (18 mm.); n^{25}_D 1.4750; d^{25}_{25} 0.9557; M_D calcd. 72.03, found 73.67, exaltation 1.64.

Anal. Calcd. for $C_{15}H_{23}O_2N$: N, 5.62. Found: N, 5.52.

VI (7.5 g.) was shaken with 75 cc. of concd. ammonia for twenty hours. Extraction with ether and distillation gave 2.5 g. (54%) of *unsym-n*-butylallylacetone, b. p. 190–191°; n^{25}_D 1.4345; m. p. of the 2,4-dinitrophenylhydrazone and mixed m. p. with the known sample described below 46–47°.

***unsym-n*-Butylallylacetone.**—The alkylation of ethyl allylacetoacetate (51 g.) with butyl iodide gave 22 g. (32%) of ethyl butylallylacetoacetate, b. p. 138–139° (22 mm.); n^{25}_D 1.4438; d^{25}_{25} 0.9512; M_D calcd. 63.45, found 63.35.

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 69.00; H, 9.80. Found: C, 69.10; H, 10.04.

The above ester (19 g.) was refluxed with 180 cc. of 5% potassium hydroxide solution for four days. Extraction and distillation gave a poor yield (3.2 g.) of *unsym-n*-butylallylacetone, b. p. 90–91.5° (21 mm.); n^{25}_D 1.4340; d^{25}_{25} 0.8463; M_D calcd. 47.94, found 47.60.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.73; H, 11.95.

The 2,4-dinitrophenylhydrazone after recrystallization had m. p. 47.5–49°.

Anal. Calcd. for $C_{16}H_{22}O_4N_4$: N, 16.76. Found: N, 16.78.

Ethyl (1,3-Dimethyl-1-butenyl)-allylcyanoacetate (VII).—Treatment of ethyl (1,3-dimethyl-butylidene)-cyanoacetate (48.8 g.) with sodium ethoxide and allyl bromide in the usual manner gave 37 g. (63%) of VII, after purification b. p. 100–101° (1.5 mm.); n^{25}_D 1.4548; d^{25}_{25} 0.9455; M_D calcd. 67.41, found 67.70.

Anal. Calcd. for $C_{14}H_{21}O_2N$: N, 5.95. Found: N, 5.89.

Ethyl (1-Methyl-2-isopropyl-4-pentenylidene)-cyanoacetate (VIII).—For rearrangement 18 g. of VII was heated a total of nine hours at 170°. Distillation gave 14.6 g. of VIII, b. p. 165–167° (24 mm.); n^{25}_D 1.4760; d^{25}_{25} 0.9641; M_D calcd. 67.41, found 69.04, exaltation 1.63.

Anal. Calcd. for $C_{14}H_{21}O_2N$: N, 5.95. Found: N, 5.95.

VIII (6 g.) on shaking with 60 cc. of concd. ammonia for twelve hours, followed by extraction and distillation, gave 1.9 g. (53%) of *unsym*-isopropylallylacetone, b. p. 67–68° (18 mm.); n^{25}_D 1.4305; m. p. of the 2,4-dinitrophenylhydrazone and mixed m. p. with a known sample 77–78.5°.

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[14] Cornubert, *Ann. Chim.*, [9] **16**, 147 (1921).

[15] Brühl, *J. prakt. Chem.*, **50**, 132 (1894).

Anal. of the 2,4-dinitrophenylhydrazone. Calcd. for $C_{16}H_{20}O_4N_4$: N, 17.49. Found: N, 17.44.

unsym-**Isopropyl Allylacetone.**—Ethyl allylacetoacetate (34 g.) was converted to the sodium enolate with sodium ethoxide and refluxed for one-half hour with isopropyl iodide. Although the reaction was incomplete, the reaction was stopped to avoid extensive cleavage by alcoholysis. The low boiling fractions of the product, which boiled over a 10° range, probably due to contamination with ethyl α-allylisovalerate, were combined, stirred with 5% potassium hydroxide for one-half hour and redistilled. The total yield of ethyl isopropylallylacetoacetate was 19 g. (45%), b. p. 118–120° (17 mm.); n^{25}_{D} 1.4491; d^{25}_{25} 0.9701; M_D calcd. 58.83, found 58.88.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.68; H, 9.54.

The above ester (17 g.) was refluxed with 180 cc. of 5% potassium hydroxide for four days. Extraction and distillation gave a poor yield (2.2 g., 20%) of *unsym*-isopropylallylacetone, b. p. 77–79° (25 mm.); n^{25}_{D} 1.4301; m. p. of the 2,4-dinitrophenylhydrazone 76–77°. In order to obtain a pure specimen of the ketone for analysis, the samples prepared by synthesis and cleavage were combined and redistilled; b. p. 168–169°; n^{25}_{D} 1.4303; d^{25}_{25} 0.8520; M_D calcd. 43.32, found 42.66.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.95; H, 11.51.

Ethyl (1-Phenylvinyl)-allylcyanoacetate (IX).—Ethyl (1-phenylethylidene)-cyanoacetate[16] (54 g.) was alkylated with allyl bromide by the usual method. In order to prevent rearrangement it was necessary to distill the product in very high vacuum. After one distillation the ester was shaken with 20% sodium bisulfite for thirty-six hours to remove any alkylidene ester, and again distilled in high vacuum; yield 40.7 g. (64%), b. p. 101° [about 1×10^{-5} mm. (pressure of the pumping system read on a McLeod gage)]; n^{25}_{D} 1.5225; d^{25}_{25} 1.0480; M_D calcd. 73.04, found 74.58, exaltation 1.54.

Anal. Calcd. for $C_{16}H_{17}O_2N$: N, 5.49. Found: N, 5.28.

Ethyl (1-Phenyl-4-pentenylidene)-cyanoacetate (X).—IX failed to give pure X when heated at 200°. When IX (31.6 g.) was heated for seven hours at 170°, 24.8 g. of X was obtained; b. p. 138–139° (0.5 mm.); n^{25}_{D} 1.5375; d^{25}_{25} 1.0526; M_D calcd. 73.04, found 76.03, exaltation 2.99.

Anal. Calcd. for $C_{16}H_{17}O_2N$: N, 5.49. Found: N, 5.34.

X (16.5 g.) was shaken with concd. ammonia for thirty-six hours. Extraction and distillation gave 4 g. (39%) of ω-allylacetophenone, b. p. 136–137° (24 mm.); semicarbazone, m. p. 157–157.5°; oxime m. p. 53–53.5°. The constants reported by Helferich and Lecher[17] for this ketone are: b. p. 135–138° (24 mm.); semicarbazone m. p. 156–157°; oxime m. p. 53–54°.

Ethyl (1-Ethylpropenyl)-allylcyanoacetate (XI).—Ethyl (1-ethylpropylidene)-cyanoacetate (45.3 g.) was alkylated with allyl bromide, yielding 48.5 g. (88%) of XI; after purification b. p. 90–91° (1 mm.); n^{25}_{D} 1.4617; d^{25}_{25} 0.9704; M_D calcd. 62.79, found 62.84.

Anal. Calcd. for $C_{13}H_{19}O_2N$: N, 6.33. Found: N. 6.23.

Ethyl (1-Ethyl-2-methyl-4-pentenylidene)-cyanoacetate (XII).—XI (23 g.) heated for seven hours at 200° gave 16 g. of XII, b. p. 162–163° (25 mm.); n^{25}_{D} 1.4771; d^{25}_{25} 0.9773; M_D calcd. 62.79, found 64.18, exaltation 1.39.

Anal. Calcd. for $C_{13}H_{19}O_2N$: N, 6.33. Found: N, 6.30.

XII (10 g.) was shaken with 100 cc. of concd. ammonia for twenty-four hours. Extraction and distillation gave 4.1 g. (72%) of α-allyl diethyl ketone, b. p. 153.5–154°; n^{25}_{D} 1.4252; d^{25}_{25} 0.8369; M_D calcd. 38.70, found 38.69.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.17; H, 11.40.

The 2,4-dinitrophenylhydrazone of this ketone (recrystallized from alcohol) had m. p. 79.5–81°.

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.29. Found: N, 18.14.

It was identical in m. p. and mixed m. p. with the derivative of the synthetic ketone described below.

α-Allyl Diethyl Ketone.—Diethyl ketone (30.1 g.) was converted to the sodium derivative by addition to a suspension of freshly prepared sodamide in ether and alkylated with allyl bromide according to the general method of Haller and Bauer.[18] Fractionation gave 24.7 g. (56%) of α-allyl diethyl ketone, b. p. 153–156°; m. p. of the 2,4-dinitrophenylhydrazone 79.5–80°.

1-Cyclohexenyl Allylmalononitrile (XIII).—Cyclohexylidene malononitrile (36.5 g.) was converted to the sodium derivative with alcoholic sodium ethoxide and alkylated with allyl bromide in the same manner as the cyanoacetic esters. A preliminary preparation had shown that XIII rearranges very readily during distillation, so the product was shaken with 20% sodium bisulfite before distilling, to remove any cyclohexylidene malononitrile which might be present, and distilled in high vacuum. XIII was thus obtained in 93% yield (43.5 g.); b. p. 58–60° (about 1×10^{-5} mm.); n^{25}_{D} 1.4860; d^{25}_{25} 0.9870; M_D calcd. 54.14, found 54.34.

Anal. Calcd. for $C_{12}H_{14}N_2$: N, 15.04. Found: N, 15.14.

2-Allyl Cyclohexylidene Malononitrile (XIV).—XIII (25.6 g.) was heated for one and one-half hours at 175° and then fractionated. The rearrangement was complete, for all of the fractions had the same refractive index. The yield of XIV was 24.6 g. (96%); b. p. 109–110° (0.5 mm.); n^{25}_{D} 1.5143; d^{25}_{25} 0.9970; M_D calcd. 54.14, found 56.44, exaltation 2.30.

Anal. Calcd. for $C_{12}H_{14}N_2$: N, 15.04. Found: N, 14.98.

XIV (21 g.) was shaken with 90 cc. of concd. ammonia for two days. On extraction and distillation 12.4 g. of XIV was recovered, while 2.6 g. (41% based on XIV consumed) of 2-allylcyclohexanone was obtained, b. p. 108° (26 mm.). The oxime, m. p. 70.5–71.0°, was identical in m. p. and mixed m. p. with the known sample previously described.

1-Ethyl-propenyl Allylmalononitrile (XV).—1-Ethylpropylidene malononitrile (33.6 g.) was alkylated by treatment with sodium ethoxide and allyl bromide. As in the

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[16] Scheiber and Meisel, *Ber.*, **48**, 260 (1915).

[17] Helferich and Lecher, *ibid.*, **54**, 930 (1921).

[18] Haller and Bauer, *Ann. chim.*, [8] **29**, 335 (1913).

preceding alkylation, the reaction occurred so rapidly that it was not necessary to heat the mixture to boiling. The product was extracted, shaken overnight with sodium bisulfite, and distilled in high vacuum. The yield of XV was 35.4 g. (81%); b. p. 40–42° (about 1×10^{-5} mm.); $n^{25}\text{D}$ 1.4639; $d^{25}{}_{25}$ 0.9282; *M*D calcd. 51.72, found 51.95.

Anal. Calcd. for $C_{11}H_{14}N_2$: N, 16.08. Found: N, 15.97.

(1-Ethyl-2-methyl-4-pentenylidene)-malononitrile (XVI).—XV (22.2 g.) on heating at 150° for four hours gave a quantitative yield of XVI, b. p. 148–149° (25 mm.); $n^{25}\text{D}$ 1.4839; $d^{25}{}_{25}$ 0.9310; *M*D calcd. 51.72, found 53.70, exaltation 1.98.

Anal. Calcd. for $C_{11}H_{14}N_2$: N, 16.08. Found: N, 16.09.

XVI (11.8 g.) on shaking with 100 cc. of concd. ammonia for twenty-four hours gave 3 g. (35%) of α-allyl diethyl ketone; m. p. of the 2,4-dinitrophenylhydrazone and mixed m. p. with a known sample 80–80.5°.

Ethyl Propenylallylmalonate (XVII).—Ethyl propylidenemalonate (50 g.) was alkylated with allyl bromide, following the procedure previously used for primary alkylidene malonic esters.[9] The product (XVII) was purified by fractionation through a Widmer column, yield 45.5 g. (76%), b. p. 79–80° (1 mm.): $n^{25}\text{D}$ 1.4480; $d^{25}{}_{25}$ 0.9949; *M*D calcd. 64.62, found 64.85.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.78; H, 8.41.

Ethyl (2-Methyl-4-pentenylidene)-malonate (XVIII).—XVII (28.2 g.) was heated at 200° for eight hours, giving 25.4 g. (90%) of XVIII, b. p. 144–145° (18 mm.); $n^{25}\text{D}$ 1.4536; $d^{25}{}_{25}$ 0.9931; *M*D calcd. 64.62, found 65.62, exaltation 1.00.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.04; H, 8.39.

Proof of Structure of XVIII.—XVIII was reduced quantitatively by hydrogen in the presence of palladinized charcoal to ethyl (2-methyl-pentyl)-malonate (11.3 g. or 96% from 11.7 g. of XVIII); b. p. 146–147° (24 mm.); $n^{25}\text{D}$ 1.4268. The reduced ester (11 g.) was condensed with urea in the presence of alcoholic sodium ethoxide in the usual manner.[19] The product, 5-(2-methyl-pentyl)-barbituric acid, was recrystallized from alcohol; yield 7.5 g. (79%); m. p. 200.5–201°.

Known samples of ethyl (2-methyl-pentyl)-malonate and the corresponding barbituric acid were prepared for comparison with the specimens derived from XVIII.

2-Methylpentanal was prepared in poor yield by the hydrogenation of α-methyl-β-ethylacrolein in the presence of palladinized charcoal[20] in alcohol solution. The reduction proceeded smoothly, but the product proved to be very difficult to separate from the alcohol used as a solvent. 2-Methylpentanal (24 g.) was condensed with ethyl malonate (40 g.) in the presence of 1 cc. of piperidine, 2.9 cc. of glacial acetic acid and 40 cc. of benzene by refluxing the mixture under a constant water separator until no more water was formed (5.5 hours). The solution was cooled, washed with dilute sodium chloride solution and distilled. The yield of ethyl (2-methylpentylidene)-malonate was 45.2 g. (78%); b. p. 147–149° (23 mm.); $n^{25}\text{D}$ 1.4439; $d^{25}{}_{25}$ 0.9724; *M*D calcd. 65.09, found 66.38, exaltation 1.29.

Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.43; H, 9.33.

The hydrogenation of ethyl (2-methyl-pentylidene)-malonate (45.2 g.) in the presence of palladinized charcoal in alcohol solution gave ethyl (2-methyl-pentyl)-malonate (42.3 g., 92%); b. p. 146–147° (24 mm.); $n^{25}\text{D}$ 1.4263; $d^{25}{}_{25}$ 0.9566; *M*D calcd. 65.56, found 65.67.

Anal. Calcd. for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 64.09; H, 10.11.

Condensation of the above ester (24.4 g.) with urea in the presence of alcoholic sodium ethoxide gave a known sample of 5-(2-methyl-pentyl)-barbituric acid; m. p. after recrystallization from alcohol 201–201.5°; yield 16.8 g. (79%). A mixture of this known acid and the sample derived from the reduction product of XVIII also melted at 201–201.5°.

Anal. Calcd. for $C_{10}H_{16}O_3N_2$: N, 13.20. Found: N, 13.21.

Ethyl (2-Ethyl-4-pentenylidene)-malonate (XX).—Ethyl (1-butenyl)-allylmalonate (XIX)[11] (30.1 g.) was heated at 200° for a total of ten hours, producing 20.5 g. (68%) of XX, b. p. 143–144° (13 mm.); $n^{25}\text{D}$ 1.4559; $d^{25}{}_{25}$ 0.9884; *M*D calcd. 69.24, found 70.10, exaltation 0.86.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.15; H, 8.72. Found: C, 66.18; H, 8.68.

Proof of Structure of XX.—XX (8.1 g.) was hydrogenated in the presence of palladinized charcoal in alcohol solution to ethyl (2-ethyl-pentyl)-malonate; yield 6.6 g. (81%), b. p. 157–159° (28 mm.); $n^{25}\text{D}$ 1.4299. The hydrogenation product (6 g.) on condensation with urea in the usual manner gave 3.1 g. (60%) of 5-(2-ethylpentyl)-barbituric acid, crystals from alcohol, m. p. 176.5–177°.

Known samples of ethyl (2-ethyl-pentyl)-malonate and barbituric acid were prepared for comparison as follows. Ethyl propylmalonate was prepared by the reduction of ethyl propylidenemalonate and converted into ethyl ethylpropylmalonate by alkylation with ethyl bromide. The resulting dialkylmalonic ester was reduced (with simultaneous loss of a carbethoxyl group) with hydrogen in the presence of copper–barium chromite catalyst at 250° according to the method of Connor and Adkins.[21] The product, 2-ethylpentanol, and the corresponding alkyl bromide into which it was converted have both been described previously.[22] The 2-ethylpentyl bromide so obtained (11.6 g.) was added to the sodium enolate prepared from 10.4 g. of ethyl malonate and refluxed for six hours. After diluting the reaction mixture with water, extracting with benzene and distilling, 10.5 g. (63%) of ethyl (2-ethyl-pentyl)-malonate was obtained, b. p. 94–95° (0.5 mm.); $n^{25}\text{D}$ 1.4298; $d^{25}{}_{25}$ 0.9549; *M*D calcd. 70.18, found 70.07.

Anal. Calcd. for $C_{14}H_{26}O_4$: C, 65.08; H, 10.15. Found: C, 65.05; H, 10.36.

Condensation of the above ester (8.6 g.) with urea in the usual manner gave 5.5 g. (73%) of 5-(2-ethyl-pentyl)-

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[19] Fischer and Dilthey, *Ann.*, **335**, 338 (1904).

[20] Hartung, THIS JOURNAL, **50**, 3372 (1928).

[21] Connor and Adkins, *ibid.*, **54**, 4687 (1932).

[22] Levene, Rothen, Meyer and Kuna, *J. Biol. Chem.*, **115**, 401 (1936).

barbituric acid, m. p. and mixed m. p. with the acid obtained from the reduction product of XX 176.5–177°.

Anal. Calcd. for $C_{11}H_{18}O_3N_2$: N, 12.38. Found: N, 12.43.

Ethyl Isopentenyl Allylmalonate (XXI).—Ethyl isopentylidene malonate (57 g.) on alkylation with allyl bromide yielded 61.9 g. (92%) of XXI, b. p. 111–112° (2 mm.); $n^{25}D$ 1.4437; d^{25}_{25} 0.9615; *M*D calcd. 73.86; found 74.31.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 67.16; H, 9.15.

When XXI was heated for five hours and then two hours more at 200°, the refractive index increased by only 0.0005 unit during the latter period. Fractionation gave four fractions varying in b. p. from 146 to 151° (15 mm.), and in $n^{25}D$ from 1.4508 to 1.4581. Further heating of the combined fractions gave similar mixtures, from which a pure rearrangement product could not be isolated. Mixtures were also obtained when XXI was heated at 175°, while at 145° no rearrangement occurred.

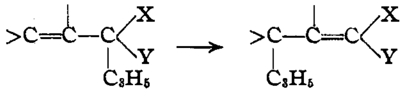
Ethyl 1-Cyclohexenyl Allylmalonate (XXII).—Ethyl 1-cyclohexenylmalonate[23] (80.7 g.) was converted into its sodium enolate with alcoholic sodium ethoxide and alkylated with allyl bromide in the usual manner. The crude product contained an impurity which was removed by shaking with concd. aqueous ammonia, fractionating, again shaking with ammonia and refractionating. The yield of XXII was 39.1 g. (46%), b. p. 109° (0.5 mm.); $n^{25}D$ 1.4742; d^{25}_{25} 1.0369; *M*D calcd. 76.28, found 76.23.

Anal. Calcd. for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.72; H, 8.75.

When XXII was heated at 200° for six to twelve hours, a mixture of substances was formed from which the pure rearrangement product could not be separated by fractionation. When the crude isomerization product was shaken with concd. ammonia for a week, a very small amount of 2-allylcyclohexanone was formed. The ketone was isolated by extraction and distillation, and identified by conversion into the oxime, m. p. and mixed m. p. with a known sample 70–70.5°.

Summary

Ten compounds containing structural elements which are represented in the following partial formulas have been shown to isomerize smoothly in the manner indicated on heating to temperatures between 135 and 200°.



(X and Y = CN or COOEt). The double bond may be either acyclic or alicyclic. Kinetic studies have shown that the order of decreasing ease of rearrangement is: malononitriles > cyanoacetic esters > malonic esters. Nine of the ten isomerizations follow the first order kinetic equation, suggesting an intra- rather than an intermolecular mechanism of rearrangement.

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[23] Kon and Speight, *J. Chem. Soc.*, 2731 (1926); Hugh and Kon, *ibid.*, 778 (1930).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Rearrangement of Allyl Groups in Three-Carbon Systems. II[1]

BY ARTHUR C. COPE,[2] CORRIS M. HOFMANN AND ELIZABETH M. HARDY

The first report of the rearrangement (α,γ-shift) of an allyl group in a three-carbon system[3] pointed out the structural analogy of this reaction to the Claisen rearrangement. The results described in the preceding paper[4] indicate that the rearrangement is quite general for suitably activated three-carbon systems, just as the Claisen rearrangement is general for the $>C{=}C{-}O{-}C_3H_5$ system. This communication describes work undertaken to determine whether substituted allyl groups undergo inversion[5] in the isomerization.

A test of the intra- or intermolecular nature of the reaction was also made, by determining whether an interchange of groups takes place during the simultaneous rearrangement of mixtures.

The occurrence of inversion during the rearrangement was established by preparing ethyl isopropenyl crotylmalonate (I) and ethyl (1-methyl propenyl)-crotylcyanoacetate (II), rearranging these two esters, and determining the structures of the rearrangement products. Preliminary efforts to employ the corresponding esters substituted by cinnamyl rather than crotyl groups failed, for the cinnamyl compounds decomposed during distillation and could not be purified.

The esters I and II were prepared by alkylating ethyl isopropylidenemalonate[6] and ethyl (1-

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[3] Cope and Hardy, THIS JOURNAL, **62**, 441 (1940).

[4] Cope, Hoyle and Heyl, *ibid.*, **63**, 1843 (1941).

[5] *Cf.* Tarbell, *Chem. Rev.*, **27**, 500, 516 (1940), for a discussion of inversion in the Claisen rearrangement.

[6] Cope and Hancock, THIS JOURNAL, **60**, 2644 (1938).